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# Large-scale preparation of nanoporous TiO<sub>2</sub> film on titanium substrate with improved photoelectrochemical performance

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## Abstract

Fabrication of three-dimensional TiO<sub>2</sub> films on Ti substrates is one important strategy to obtain efficient electrodes for energy conversion and environmental applications. In this work, we found that hierarchical porous TiO<sub>2</sub> film can be prepared by treating H<sub>2</sub>O<sub>2</sub> pre-oxidized Ti substrate in TiCl<sub>3</sub> solution followed by calcinations. The formation process is a combination of the corrosion of Ti substrate and the oxidation hydrolysis of TiCl<sub>3</sub>. According to the characterizations by scanning electron microscopy (SEM), X-ray diffraction (XRD), and diffuse reflectance spectroscopy (DRS), the anatase phase TiO<sub>2</sub> films show porous morphology with the smallest diameter of 20 nm and possess enhanced optical absorption properties. Using the porous film as a working electrode, we found that it displays efficient activity for photoelectrocatalytic decolorization of rhodamine B (RhB) and photocurrent generation, with a photocurrent density as high as 1.2 mA/cm<sup>2</sup>. It represents a potential method to fabricate large-area nanoporous TiO<sub>2</sub> film on Ti substrate due to the scalability of such chemical oxidation process.

**Keywords:** Nanoporous TiO<sub>2</sub> film; Titanium substrate; Photocurrent; Photoelectrocatalysis

## Background

In recent years, TiO<sub>2</sub> has been widely studied and applied in diverse fields, such as photocatalysis, dye-sensitized solar cell, self-cleaning surface, sensor, and biomedicine [1-6]. It is well known that TiO<sub>2</sub> nanoparticles have the potential to remove recalcitrant organic pollutants in wastewater. However, it is prerequisite to produce immobilized TiO<sub>2</sub> photocatalysts with highly efficient activity by scale-up methods. Recently, considerable efforts have been taken to use metallic titanium as the precursor to develop three-dimensional TiO<sub>2</sub> films with controllable ordered morphologies, such as nanotubes [7], nanorods [8], nanowires [9], and nanopores [10]. The *in situ*-generated TiO<sub>2</sub> films over titanium substrates possess such advantages as stable with low carbon residual, excellent mechanical strength, and well electron conductivity, which make them suitable to be used as electrodes for photoelectrochemical-related applications [6,11]. Although a well-defined structural nanotube or nanoporous TiO<sub>2</sub> film on metallic Ti can

be synthesized by an anodic method [6,7,10-13], it is still a big challenge to scale up the production of such TiO<sub>2</sub> film due to the limitation of electrochemical reactor and the high energy consumption. Chemical oxidation methods by treating titanium substrates in oxidation solutions are more scalable for various applications. By soaking titanium substrates in H<sub>2</sub>O<sub>2</sub> solution followed with calcinations, titania nanorod or nanoflower films can be obtained [8,14]. However, the film always displays discontinuous structure with many cracks, and its thickness is less than 1 μm [8,15]. Both of these would result in a low photoelectrochemical performance. With the addition of concentrated NaOH in the H<sub>2</sub>O<sub>2</sub> solution, a porous nanowire TiO<sub>2</sub> film can be achieved after an ionic exchange with protons and subsequent calcinations [9]. Employing NaOH and organic solvent as the oxidation solution and elevating the treating temperature, Ti substrate would completely transform into free-standing TiO<sub>2</sub> nanowire membranes [16]. However, the disappearance of Ti substrate makes this membrane impossible to serve as an electrode.

Compared to titanium alkoxides or TiCl<sub>4</sub>, there are much fewer reports on the synthesis of TiO<sub>2</sub> nanostructure

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with the precursor of  $\text{TiCl}_3$ . Normally, anatase  $\text{TiO}_2$  film can be fabricated via the anodic oxidation hydrolysis of  $\text{TiCl}_3$  solution [17,18]. Recently, Hosono et al. synthesized rectangular parallelepiped rutile  $\text{TiO}_2$  films by hydrothermally treating  $\text{TiCl}_3$  solution with the addition of a high concentration of  $\text{NaCl}$  [19], and Feng et al. developed  $\text{TiO}_2$  nanorod films with switchable superhydrophobicity/superhydrophilicity transition properties via a similar method [20]. Moreover, a hierarchically branched  $\text{TiO}_2$  nanorod film with efficient photon-to-current conversion efficiency can be achieved by treating the nanorod  $\text{TiO}_2$  film in  $\text{TiCl}_3$  solution [21]. However, all of these nanostructural  $\text{TiO}_2$  films from  $\text{TiCl}_3$  solution were grown over glass or alumina substrates. Fabricating nanostructural  $\text{TiO}_2$  films over metallic Ti substrates is a promising way to providing high-performance photoresponsible electrodes for photoelectrochemical applications. The obstacle for starting from Ti substrates and  $\text{TiCl}_3$  solution must be the corrosion of metallic Ti at high temperatures in the HCl solution, which is one of the components in  $\text{TiCl}_3$  solution. However, the corrosion could also be controlled and utilized for the formation of porous structures. According to reports, the general method to prepare nanoporous  $\text{TiO}_2$  film on Ti substrate is through anodic oxidation and post-sonication [10,12]. In this contribution, we proposed a facile way to fabricate nanoporous  $\text{TiO}_2$  films by post-treating the  $\text{H}_2\text{O}_2$ -oxidized  $\text{TiO}_2$  film in a  $\text{TiCl}_3$  solution. The as-prepared nanoporous  $\text{TiO}_2$  film display homogeneous porous structure with enhanced optical adsorption property and photoelectrocatalytic performance, which indicates that the film is promising in the applications of water purification and photoelectrochemical devices.

## Methods

Cleansed Ti plates (99.5% in purity, Baoji Ronghao Ti Co. Ltd., Shanxi, China) with sizes of  $1.5 \times 1.5 \text{ cm}^2$  were pickled in a 5 wt% oxalic acid solution at  $100^\circ\text{C}$  for 2 h, followed by rinsing with deionized water and drying in an air stream. The nanoporous  $\text{TiO}_2$  film was prepared by a two-step oxidation procedure. Briefly, the pre-treated Ti plate was firstly soaked in a 15 mL 20 wt%  $\text{H}_2\text{O}_2$  solution in a tightly closed bottle, which was maintained at  $80^\circ\text{C}$  for 12 h. The treated Ti plate was rinsed gently with deionized water and dried. Then, it was immersed in a 10 mL  $\text{TiCl}_3$  solution (0.15 wt%) at  $80^\circ\text{C}$  for 2 h. Finally, the film was cleaned, dried, and calcined at  $450^\circ\text{C}$  for 2 h. The obtained nanoporous  $\text{TiO}_2$  film was designed as NP-TiO<sub>2</sub>. Two control samples were synthesized, including the one designed as TiO<sub>2</sub>-1, which was obtained by directly calcining the cleansed Ti plate, and the other named as TiO<sub>2</sub>-2, which was prepared by one-step treatment of the Ti plate in a  $\text{TiCl}_3$  solution.

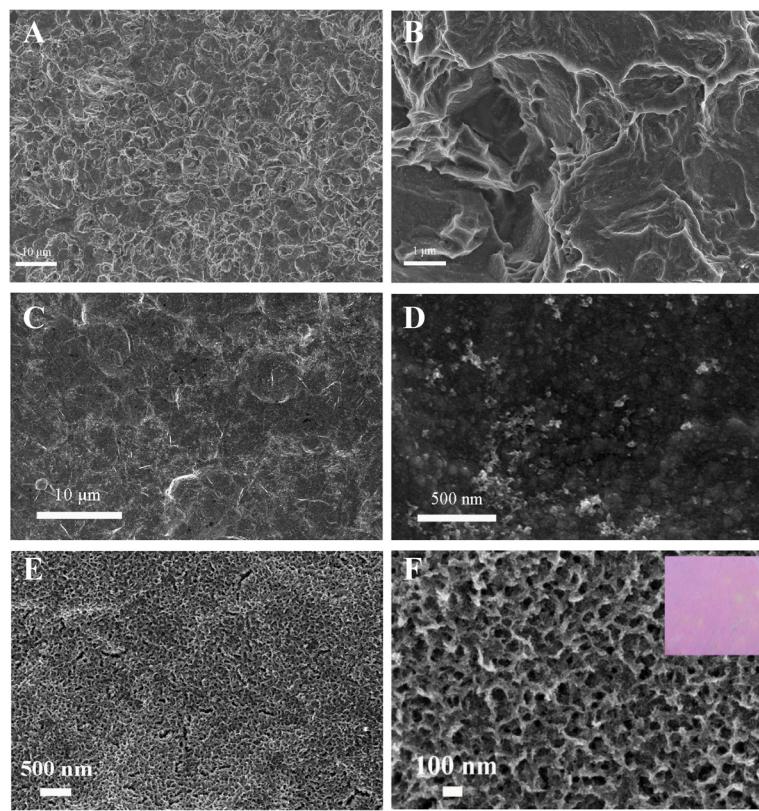
The surface morphology of  $\text{TiO}_2$  films was observed using a field emission scanning electron microscope (SEM; Zeiss Ultra 55, Oberkochen, Germany). The crystal phases were analyzed using a powder X-ray diffractometer (XRD; D8 Advance, Bruker, Ettlingen, Germany) with Cu K $\alpha$  radiation, operated at 40 kV and 36 mA ( $\lambda = 0.154056 \text{ nm}$ ). UV-vis diffuse reflectance spectra (DRS) were recorded on a Lambda 950 UV/Vis spectrophotometer (PerkinElmer Instrument Co. Ltd., Waltham, MA, USA) and converted from reflection to absorption by the Kubelka-Munk method.

Photoelectrochemical test systems were composed of a CHI 600D electrochemistry potentiostat, a 500-W xenon lamp, and a homemade three-electrode cell using as-prepared  $\text{TiO}_2$  films, platinum wire, and a Ag/AgCl as the working electrode, counter electrode, and reference electrode, respectively. A 0.5 M  $\text{Na}_2\text{SO}_4$  solution purged with nitrogen was used as electrolyte for all of the measurements.

The photocatalytic or photoelectrocatalytic degradation of rhodamine B (RhB) over the NP-TiO<sub>2</sub> film was carried out in a quartz glass cuvette containing 20 mL of RhB solution ( $\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$ , initial concentration 5 mg/L). The pH of the solution was buffered to 7.0 by 0.1 M phosphate. The solution was stirred continuously by a magnetic stirrer. Photoelectrocatalytic reaction was performed in a three-electrode system with a 0.5-V anodic bias. The exposed area of the electrodes under illumination was  $1.5 \text{ cm}^2$ . Concentration of RhB was measured by spectrometer at the wavelength of 554 nm.

## Results and discussion

Figure 1 shows the surface morphologies of films obtained by different procedures. The control sample TiO<sub>2</sub>-1 is obtained by the calcination of the pickled Ti plate at  $450^\circ\text{C}$  for 2 h. The typical coarse surface formed from the corrosion of Ti plate in oxalic solution can be observed (Figure 1A,B). By oxidation at a high temperature, the surface layer of titanium plate transformed into  $\text{TiO}_2$ . However, the surface morphology shows negligible change. The film of TiO<sub>2</sub>-2, which is synthesized by directly treating the cleansed and pickled Ti plate in  $\text{TiCl}_3$  solution, displays smoother surface with no observable nanostructure (Figure 1C,D). Moreover, there are discernible  $\text{TiO}_2$  particles dispersing over the surface. It suggests that in the  $\text{TiCl}_3$  solution the surface morphology of Ti plate has been modified after dissolution, precipitation and deposition processes. By treating the  $\text{H}_2\text{O}_2$  pre-oxidized Ti plate in  $\text{TiCl}_3$ , the film displays a large-scale irregular porous structure, as shown in Figure 1E,F. Moreover, the appearance of NP-TiO<sub>2</sub> film is red color (as inset in Figure 1F), which is different from the normal appearance of most anodic  $\text{TiO}_2$  nanorod or nanotube films [22]. The pores are in the sizes of 50 to



**Figure 1** FE-SEM images of  $\text{TiO}_2$  films over Ti plates. **(A, B)**  $\text{TiO}_2$ -1, **(C, D)**  $\text{TiO}_2$ -2, and **(E, F)** NP- $\text{TiO}_2$  (the inset in **(F)** shows the digital picture of the NP- $\text{TiO}_2$  film).

100 nm on the surface and about 20 nm inside; the walls of the pores are in the sizes of 10 nm and show continuous connections. Such hierarchical porous structure contributes to a higher surface area of the  $\text{TiO}_2$  film. Normally, titanium suffers from corrosion in the hot HCl solution, and the corrosion rate depends on the temperature and the concentration of acid. Without pre-oxidation, the surface layer of Ti plate is exposed to be etched and dissolved in the reaction solution at a medium temperature. Simultaneously, the  $\text{TiOH}^{2+}$  and Ti(IV) polymer generated by the hydrolysis of  $\text{TiCl}_3$  would precipitate and deposit over the surface (Equations 1 and 2) so as to retard the corrosion of Ti plate and avoid the completed dissolution of Ti plate [17,19]. For the NP- $\text{TiO}_2$  film, after the first step of oxidation in  $\text{H}_2\text{O}_2$  solution, peroxy complexes coordinated to Ti(IV) have already formed, which cover most parts of the surface and be ready for further growth by the interaction with the oxidation hydrolytic products of  $\text{TiCl}_3$ . However, it is also possible that HCl solution enters the interstitial of the  $\text{TiO}_2$  nanorod film and induces etching of the substrate Ti. At the experimental temperature, the dissolution of Ti is slow. With the reorganization of Ti(IV) polymer

precursor, a porous structure forms over the Ti plate, as shown in Figure 1F.

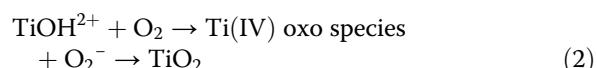
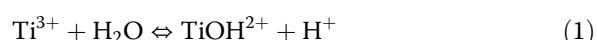
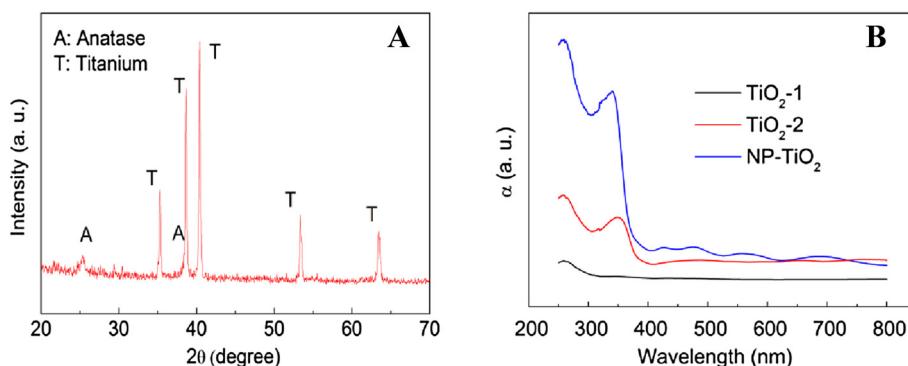


Figure 2A is the XRD pattern of NP- $\text{TiO}_2$  film. The strong diffraction peaks at about 35.2°, 38.7°, 40.4°, 53.3°, and 63.5° can be assigned to the metallic Ti (JCPDS 44-1294). At the same time, the peak at 25.3° corresponds to the (101) plane of anatase phase  $\text{TiO}_2$  (JCPDS 83-2243). Diffraction peaks of rutile or brookite cannot be found, indicating that the titania film is composed of exclusively anatase. DRS spectra were measured to analyze the optical absorption properties of the films, as shown in Figure 2B. There is almost no optical adsorption for the  $\text{TiO}_2$ -1 film, indicating that only a very thin layer of metallic Ti transforms into  $\text{TiO}_2$  after the calcination of Ti plate, and this contributes a poor photoresponse performance.  $\text{TiO}_2$ -2 film displays a typical semiconductor optical absorption with the adsorption edge at about 380 nm, corresponding to the band gap of

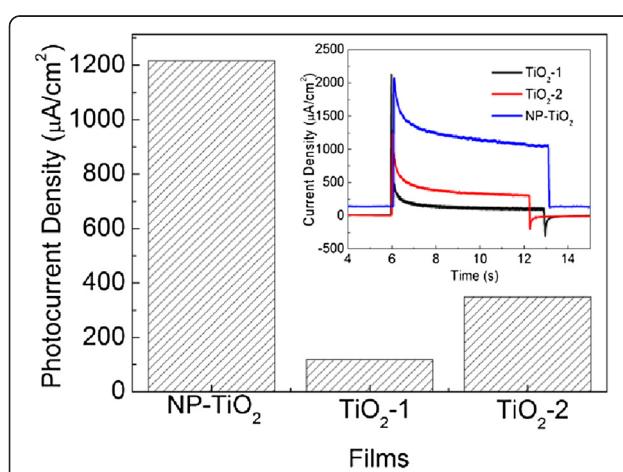


**Figure 2** XRD pattern of NP-TiO<sub>2</sub> (A) and the DRS spectra of various films (B).

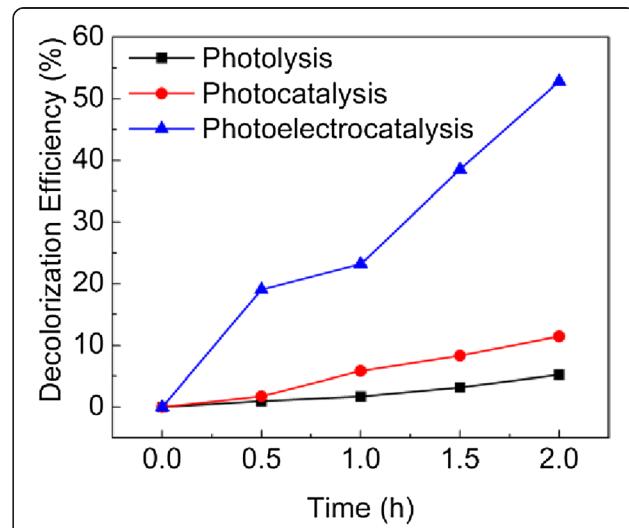
anatase TiO<sub>2</sub>. However, the absorption is relatively low, indicating that only few of TiO<sub>2</sub> nanoparticles deposit over the surface of TiO<sub>2</sub>-2 film. The strong optical absorption appearing below 400 nm for NP-TiO<sub>2</sub> film suggests a full growth of TiO<sub>2</sub> layer over the Ti plate. Moreover, several adsorption bands centered at about 480, 560, and 690 nm can be observed in the spectrum of NP-TiO<sub>2</sub> film. They possibly originated from the periodic irregular nanoporous structure. Such nanoporous structure is favorable to increase the photoresponsible performance, because the incident light that entered the porous structure would extend the interaction of light with TiO<sub>2</sub> and result in an enhanced absorption performance, which can be observed in other nanotube or photonic crystal structural TiO<sub>2</sub> films [22,23].

Using TiO<sub>2</sub> films as the working electrodes in a three-electrode system, photocurrents under irradiation with full spectrum of light source were measured and compared, as shown in Figure 3. From the current transients (inset in Figure 3), all films show anodic photocurrents

upon illumination, corresponding to the n-type photoresponse of TiO<sub>2</sub>. For TiO<sub>2</sub>-1 film, the initial anodic photocurrent spike is very strong and subsequently decays quickly. Simultaneously, a cathodic overshoot appears immediately when the light is switched off. The anodic current spike and cathodic overshoot are occasionally observed in many cases, and which is generally regarded as the indication of the surface recombination of photogenerated charges [24-26]. A decay of anodic current immediately after the initial rise of the signal when the light is switched on is attributed to photogenerated electron transfer to the holes trapped at the surface states or the intermediates which originated from the reaction of holes at the semiconductor surface. With the accumulation of the intermediates, the electrons are trapped by the surface states, resulting in an anodic current spike. Owing to the same reason, the intermediates or trapped holes would induce a cathodic overshoot when switching off the light. The obvious



**Figure 3** A comparison of photocurrent density of various films. The inset shows a comparison of the current transients (applied potential: 0.2 V vs. Ag/AgCl).



**Figure 4** RhB decolorization as a function of time under various conditions.

strong spike for the illuminated  $\text{TiO}_2$ -1 film suggests the slow consumption of holes and the corresponding oxidation process, which is related to the activity of the surface  $\text{TiO}_2$  layer. The poor crystallinity, large  $\text{TiO}_2$  particles, and the small amount of  $\text{TiO}_2$  in the directly oxidized film would result in the poor photoelectrochemical performance. However, the transient of NP- $\text{TiO}_2$  film is different, displaying much smaller anodic current spike and more stable photocurrent. The photocurrent density is calculated as the difference of the current density upon illumination at the center time and in the dark, which is shown as a graph in Figure 3. NP- $\text{TiO}_2$  film possesses the highest photocurrent density, which is about  $1.2 \text{ mA/cm}^2$ , significantly higher than the corresponding  $\text{TiO}_2$ -1 and  $\text{TiO}_2$ -2 films. The efficient photoelectrochemical performance can be attributed to the porous structure of NP- $\text{TiO}_2$  film, in which the interaction time between  $\text{TiO}_2$  and light would be increased due to the trapped photons inside the pores, corresponding to its enhanced optical absorption.

The performance of the NP- $\text{TiO}_2$  film was further tested by photoelectrocatalytic degradation of RhB solutions. The decolorization of RhB by photolysis is low, only 5.2% reduction observed after 2 h of irradiation (Figure 4). Without an applied bias, by illuminating the solution with the NP- $\text{TiO}_2$  film, the decolorization efficiency only improved to about 11%. This low photocatalytic efficiency of the film could be attributed to the too small active area of the film and the phosphate in the buffered solution, which is regarded as the scavenger of radicals [27]. However, with a bias of 0.5 V vs. Ag/AgCl, the decolorization of RhB has been significantly improved, about 52.8% decolorization of RhB solution after 2 h of irradiation. Photoelectrocatalysis is a combination of photocatalysis and electrooxidation using the semiconductor films. By this method, an anodic bias on NP- $\text{TiO}_2$  film is used to drive photogenerated electrons and holes moving toward different direction, so as to suppress the recombination and promote the organic degradation [11,28]. Moreover, besides the improved optical absorption, the porous structure also contributes to a short diffusion path for RhB molecules to the active surface area. Therefore the NP- $\text{TiO}_2$  film displays efficient photoelectrocatalytic activity for organic degradation. It can be expected that the chemical oxidation method for NP- $\text{TiO}_2$  films is scalable for practical applications. With a larger active area, the NP- $\text{TiO}_2$  film is potential to be used as an efficient electrode for energy conversion and organic pollutant removal.

## Conclusions

A nanoporous  $\text{TiO}_2$  film on Ti substrate was synthesized by treating the initially  $\text{H}_2\text{O}_2$ -oxidized Ti plate in hot  $\text{TiCl}_3$  solution and followed by calcinations. The

pre-oxidation in  $\text{H}_2\text{O}_2$  solution is necessary to form such porous structure, indicating that the formation process is a combination of the corrosion of Ti substrate and the oxidation hydrolysis of  $\text{TiCl}_3$ . The film possesses exclusively anatase phase and hierarchical porous morphology, with the diameter of the inside pores as small as 20 nm. The porous  $\text{TiO}_2$  film displays enhanced optical absorption, photocurrent generation, and efficient photoelectrocatalytic activity for RhB decolorization. The generated photocurrent density can reach as high as  $1.2 \text{ mA/cm}^2$ . The chemical oxidation method for the nanoporous  $\text{TiO}_2$  film is possible to be scaled up and developed into a strategy to provide efficient  $\text{TiO}_2$  electrodes for diverse applications.

## Competing interests

The authors declare that they have no competing interests.

## Authors' contributions

ML designed the experiments. BT and YZ carried out all of the experiments. BT and ML wrote the paper. All authors read and approved the final manuscript.

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## References

1. Fujishima A, Zhang X, Tryk DA:  $\text{TiO}_2$  photocatalysis and related surface phenomena. *Surf Sci Rep* 2008, **63**:515–582.
2. Tran PD, Wong LH, Barber J, Loo JSC: Recent advances in hybrid photocatalysts for solar fuel production. *Energ Environ Sci* 2012, **5**:5902.
3. Kubacka A, Fernandez-Garcia M, Colon G: Advanced nanoarchitectures for solar photocatalytic applications. *Chem Rev* 2012, **112**:1555–1614.
4. Long MC, Wu D, Cai WM: Photoinduced hydrophilic effect and its application on self-cleaning technology. *Recent Pat Eng* 2010, **4**:189–199.
5. Cheyne R, Smith T, Trembleau L, McLaughlin A: Synthesis and characterisation of biologically compatible  $\text{TiO}_2$  nanoparticles. *Nanoscale Res Lett* 2011, **6**:1–6.
6. Zheng Q, Zhou BX, Bai J, Li LH, Jin ZJ, Zhang JL, Li JH, Liu YB, Cai WM, Zhu XY: Self-organized  $\text{TiO}_2$  nanotube array sensor for the determination of chemical oxygen demand. *Adv Mater* 2008, **20**:1044–1049.
7. Macak JM, Tsuchiya H, Taveira L, Aldabergerova S, Schmuki P: Smooth anodic  $\text{TiO}_2$  nanotubes. *Angew Chem Int Ed* 2005, **44**:7463–7465.
8. Wu JM, Zhang TW, Zeng YW, Hayakawa S, Tsuru K, Osaka A: Large-scale preparation of ordered titania nanorods with enhanced photocatalytic activity. *Langmuir* 2005, **21**:6995–7002.
9. Wu YH, Long MC, Cai WM, Dai SD, Chen C, Wu DY, Bai J: Preparation of photocatalytic anatase nanowire films by in situ oxidation of titanium plate. *Nanotechnology* 2009, **20**:185703.
10. de Tacconi NR, Chenthamarakshan CR, Yogeeswaran G, Watcharenwong A, de Zoysa RS, Basit NA, Rajeshwar K: Nanoporous  $\text{TiO}_2$  and  $\text{WO}_3$  films by anodization of titanium and tungsten substrates: influence of process variables on morphology and photoelectrochemical response†. *J Phys Chem B* 2006, **110**:25347–25355.
11. Quan X, Yang SG, Ruan XL, Zhao HM: Preparation of titania nanotubes and their environmental applications as electrode. *Environ Sci Technol* 2005, **39**:3770–3775.
12. Liu YB, Zhou BX, Bai J, Li JH, Zhang JL, Zheng Q, Zhu X, Cai WM: Efficient photochemical water splitting and organic pollutant degradation by

- highly ordered TiO<sub>2</sub> nanopore arrays. *Appl Catal B Environ* 2009, **89**:142–148.
- 13. Xu C, Song Y, Lu LF, Cheng CW, Liu DF, Fang XH, Chen XY, Zhu XF, Li DD: Electrochemically hydrogenated TiO<sub>2</sub> nanotubes with improved photoelectrochemical water splitting performance. *Nanoscale Res Lett* 2013, **8**:7.
  - 14. Wu JM, Huang B, Zeng YH: Low-temperature deposition of anatase thin films on titanium substrates and their abilities to photodegrade rhodamine B in water. *Thin Solid Films* 2006, **497**:292–298.
  - 15. Wu YH, Long MC, Cai WM: Novel synthesis and property of TiO<sub>2</sub> nano film photocatalyst with mixed phases. *J Chem Eng Chin Univ* 2010, **24**:1005–1010.
  - 16. Hu A, Zhang X, Oakes KD, Peng P, Zhou YN, Servos MR: Hydrothermal growth of free standing TiO<sub>2</sub> nanowire membranes for photocatalytic degradation of pharmaceuticals. *J Hazard Mater* 2011, **189**:278–285.
  - 17. Kavan L, O'Regan B, Kay A, Grätzel M: Preparation of TiO<sub>2</sub> (anatase) films on electrodes by anodic oxidative hydrolysis of TiCl<sub>3</sub>. *J Electroanal Chem* 1993, **346**:291–307.
  - 18. Lei Y, Zhang LD, Fan JC: Fabrication, characterization and Raman study of TiO<sub>2</sub> nanowire arrays prepared by anodic oxidative hydrolysis of TiCl<sub>3</sub>. *Chem Phys Lett* 2001, **338**:231–236.
  - 19. Hosono E, Fujihara S, Kakiuchi K, Imai H: Growth of submicrometer-scale rectangular parallelepiped rutile TiO<sub>2</sub> films in aqueous TiCl<sub>3</sub> solutions under hydrothermal conditions. *J Am Chem Soc* 2004, **126**:7790–7791.
  - 20. Feng XJ, Zhai J, Jiang L: The fabrication and switchable superhydrophobicity of TiO<sub>2</sub> nanorod films. *Angew Chem Int Ed* 2005, **44**:5115–5118.
  - 21. Cho IS, Chen Z, Forman AJ, Kim DR, Rao PM, Jaramillo TF, Zheng X: Branched TiO<sub>2</sub> nanorods for photoelectrochemical hydrogen production. *Nano Lett* 2011, **11**:4978–4984.
  - 22. Lin J, Liu K, Chen X: Synthesis of periodically structured titania nanotube films and their potential for photonic applications. *Small* 2011, **7**:1784–1789.
  - 23. Lu Y, Yu H, Chen S, Quan X, Zhao H: Integrating plasmonic nanoparticles with TiO<sub>2</sub> photonic crystal for enhancement of visible-light-driven photocatalysis. *Environ Sci Technol* 2012, **46**:1724–1730.
  - 24. Peter LM: Dynamic Aspects of Semiconductor Photoelectrochemistry. *Chem Rev* 1990, **90**:753–769.
  - 25. Long MC, Beranek R, Cai WM, Kisch H: Hybrid semiconductor electrodes for light-driven photoelectrochemical switches. *Electrochim Acta* 2008, **53**:4621–4626.
  - 26. Abrantes LM, Peter LM: Transient photocurrents at passive iron electrodes. *J Electroanal Chem Interfacial Electrochem* 1983, **150**:593–601.
  - 27. Brusa MA, Grela MA: Experimental upper bound on phosphate radical production in TiO<sub>2</sub> photocatalytic transformations in the presence of phosphate ions. *Phys Chem Chem Phys* 2003, **5**:3294.
  - 28. Jiang DL, Zhang SQ, Zhao HJ: Photocatalytic degradation characteristics of different organic compounds at TiO<sub>2</sub> Nanoporous film electrodes with mixed anatase/rutile phases. *Environ Sci Technol* 2007, **41**:303–308.

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